CHEMICAL COMPOSITION AND TOXICITY ASSESSMENT OF PYROTECHNIC OBSCURANT MUNITIONS

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ABSTRACT

The procedures to assess the toxicological and environmental impact of pyrotechnic obscurant munitions requires detailed knowledge on the mass and distribution of the chemical species produced, in order to comply with national, and international laws. This paper will describe the various techniques the UK are assembling to assess obscurant pyrotechnic munitions.

The chemical species generated in the by-products of combustion and those found in the residue following ignition, are determined by controlled laboratory tests. Combustion of the pyrotechnic composition is performed within a Parr bomb chamber, with an air atmosphere pressurised to 10^6Pa. The resultant chemical species are analysed using a combination of thermogravimetry - FTIR analysis, thermal desorption/gas chromatography/mass spectrometry, and aqueous extraction techniques. The probabilistic field trial concentration and dosages during dissemination of the obscurant screen are determined as a function of meteorological conditions and topography using the computer program SCIPUFF. Any hazard to personnel can then be assessed by comparison with exposure limits published by the UK Health and Safety Executive. The description of these analytical techniques will be illustrated by examples from the recent assessment of the L84A1 hand thrown smoke grenade.

1. INTRODUCTION

Historically, military smokes and pyrotechnics have not been subject to any statutory regulation relating to their toxicity. In view of the recognition by the UK MoD of its duty of care in health, safety and environmental issues, future procurements of obscurant munitions will be required to address these issues. To this end, a set of toxicity testing guidelines were drawn up in 1988, and subsequently revised in 1996 [1]. The revisions took into account technological advances in munition design and importantly gave consideration to the context in which the munition is to be used, distinguishing between training or operational use. The revised guidelines have been proposed to NATO and currently form the basis of future UK assessment methodology.

This paper describes the revised guidelines and the development work undertaken in support of their practical implementation. This is illustrated by means of an example, taken from the recently considered assessment of the L84A1 hand thrown smoke grenade.

It must be emphasised that the results from this study relating to the inhalation hazard from the L84A1 are subject to ratification by the UK medical/toxicological authority.

2. TOXICITY TESTING GUIDELINES

According to the revised guidelines for toxicity testing of smokes and pyrotechnic mixtures [1], the most significant toxicology aspect relates to the inhalation of the airborne components. It also states that a lesser threat is posed by cutaneous and ocular routes of exposure. In addition, environmental issues need to be considered, such as the surface deposition of chemical species leading to the poisoning of flora and fauna and contamination of water sources. However, the scope of this paper is limited to exposure via inhalation.

The assessment guidelines can be broken down into the following discrete stages:

Identification and quantification of airborne species: This can be estimated from knowledge of the composition and prediction of likely chemical reactions. However, the preferred approach is to identify and measure each species within the smoke cloud directly, by chemical analysis.

Determination of safe exposure limits: An exposure limit will be a function of factors such as frequency and duration of exposure (for example, single exposure will have a different limit to multiple long term exposures). Therefore, the proposed method of use of the obscurant munition must first be reviewed as this will input into the selection of an appropriate safety limit. To this end, the toxicity guidelines draw parallels with workplace exposure to chemical guidelines and recommend that Government specified Occupational Exposure Limits (OELs) are used as the source of exposure limits.

Determination of exposure to each chemical species: To determine exposure, the atmospheric dispersion of the obscurant cloud under a range of meteorological conditions needs to be considered. To physically conduct such assessments under a range of meteorological conditions is impractical, therefore some form of prediction must be substituted.

3. L84A1 HAND THROWN SMOKE GRENADE

The L84A1 hand thrown smoke grenade (figure 1) is in service with the British Army. The grenade contains red phosphorous as the smoke producing composition, with a payload mass of approximately 225g. The grenade is of conventional design with twist and pull safety pin and fly off lever operating a percussion ignition train. Operation is by removal of the safety pin and throwing to the location where the smoke is required. Subsequent initiation of the central burster charge disseminates the payload over an area of approximately 5m radius, giving a typical screen duration of 30 seconds. The active ingredient, in terms of screen effectiveness, is phosphoric acid (H_3PO_4), formed on the reaction between phosphorus pentoxide and moisture in the atmosphere. Therefore, humidity will affect the performance of the munition, and the safety distance.

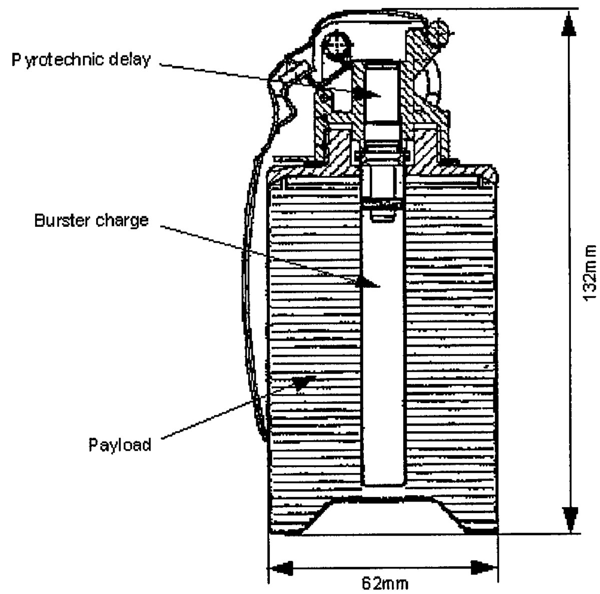

Figure 1 - L84A1 hand thrown smoke grenade

4. CHEMICAL COMPOSITION OF SMOKE CLOUD

The approach adopted in identifying and quantifying the chemical species, was by means of direct analysis of the resultant smoke cloud. Combustion of the pyrotechnic composition and containment of the resultant by-products was performed in a Parr bomb chamber [2]. After allowing the aerosol to condense, the products of reaction were collected by purging through Tenax adsorption tubes and analysed using a thermal desorption – gas chromatography – mass spectrometry technique. The condensed aerosols were collected by washing with water, and the resulting solutions were analysed using ion chromatography and direct current plasma spectrophotometry. Combustion was also carried out using thermogravimetry – Fourier transform infrared spectroscopy, to examine weight loss and to identify the major constituent of the smoke aerosols.

In total, 34 chemical species were identified. Table 1 contains a subset of the data, namely the three most abundant and the two least abundant species identified.

Chemical species	Mass
Phosphoric acid	338g
Hydrogen chloride	10g
Benzene	13.7μg
Butene	0.007μg
Butdiyne	0.004μg

Table 1 – Most and least abundant airborne products of L84A1

5. HEALTH AND SAFETY DATA

The toxicity testing guidelines recommend the use of work place occupational exposure limits (OELs) for chemicals as the basis for the safety assessment. For the purposes of this assessment, the health and safety data was extracted from [3].

[3] details exposure limits for the majority of the species identified in the analysis of the L84A1. This is given in terms of either the Short Term Exposure Limit (STEL), or the Time Weighted Average (TWA). The STEL concentration, is the specified concentration limit that can be tolerated for a time interval of 15 minutes and the TWA concentration is the concentration limit permitted for a period of 8 hours. In order that comparisons with the safety limits can be made, each of these concentration limits need to be transformed to a dosage, as this takes into account both concentration and duration of exposure. The following example considers how to make such a comparison.

The dosage D experienced at a given point (x,y,z) is defined as follows;

$$D(x,y,z) = \int_{screen\_duration} c(x,y,z,t).dt \qquad (1)$$

where c is the mass concentration at the point (x,y,z) and t is time.

The STEL is the concentration permitted for 15 minutes, therefore the dosage exposure limit, D_{STEL}, is given by;

$$D_{STEL} = C_{STEL} \,.\, 15 \text{ minutes} \qquad (2)$$

where C_{STEL} represents the STEL concentration limit.

The dosage D, at any point can thus be compared with the exposure limit dosage D_{STEL} determined above, in order to make a safety assessment.

Table 2 contains information on the three most abundant chemical species produced from the combustion of the L84A1 grenade. For each species, the OEL data (either STEL or TWA concentration limit) and an estimated concentration (assuming that the total mass of that species were produced instantly and uniformly distributed throughout a sphere of 1m radius) are given. The estimated concentration is indicative of the maximum likely concentration levels that might be experienced in the vicinity of the event. This value is an upper estimate for concentration as the payload will be dispersed over a disc on the ground, typically of radius 5m. Furthermore, the payload will burn for a given duration, whereas this calculation assumes that all the screening material is produced instantly. The use of this worst case scenario ensures that no potentially hazardous species were ignored. This process was completed for all the chemical species identified, although only the three most abundant species are shown in table 2.

Species	**Mass**	**OEL mg/m^3**	**Estimated Initial concentration mg/m^3**
Phosphoric acid	338g	2 (STEL)	8×10^4
Hydrogen chloride	10g	7.6 (STEL)	2×10^3
Benzene	13.7μg	16 (TWA)	3×10^{-3}

Table 2 – Concentration of the most abundant species produced by the L84A1

By comparison of the estimated initial concentration with the OEL figure, it is possible to rank the species in order of the hazard they pose. Any chemical species whose likely maximum concentration is orders of magnitude lower than the threshold OEL concentration can be neglected from further consideration. Any species whose maximum concentration is similar, or greater, than the limiting threshold must be considered further. This is justified

on the grounds that any controls set in place to safeguard against the greatest threats will necessarily give protection against the lesser threats.

From table 2, it can be seen that the overall assessment problem reduces to investigating two species, namely phosphoric acid and hydrogen chloride, as these are the only products with estimated concentrations greater that the appropriate STEL limit. The problem can be reduced further because not only is phosphoric acid present in greater quantities than hydrogen chloride, it is also subject to a lower OEL. Thus controls set in place for phosphoric acid will necessarily be sufficient for hydrogen chloride.

According to [3], for phosphoric acid;

$$C_{STEL} = 2\ mg.m^{-3} \tag{3}$$

Thus the STEL dosage limit for phosphoric acid can be calculated according to equation 2;

$$D_{STEL} = 0.0018\ kg.m^{-3}.s \tag{4}$$

It is worth noting that the actual values chosen for safe exposure limits will depend on the proposed mode of use of the munition. However, once concentration/dosage maps have been generated, the variation of safety distance with exposure limit and mode of operation can be explored. The scope of this paper purely considers safety in accordance with the STEL threshold.

6. ATMOSPHERIC TRANSPORT

The previous section determined the concentration and dosage limits for the primary inhalation hazard, which was shown to be phosphoric acid. To physically conduct a toxicological assessment for the range of meteorological conditions in which the munition will be used is impractical. Therefore, to assess the dispersion of the hazardous species the use of numerical simulation is invoked, namely the SCIPUFF model.

SCIPUFF (Second Order Closure Integrated PUFF) is a Lagrangian transport and diffusion model. This model is a component of the Hazard Prediction and Assessment Capability (HPAC) developed by the Defense Threat Reduction Agency (DTRA) of the US. HPAC is primarily designed for the hazard assessment of nuclear, chemical and biological incidents and is claimed to be good for 'nearly any' atmospheric incident. Chemical, biological and nuclear materials can be hazardous in extremely low concentrations, thus the model is designed to predict atmospheric transport from releases over large time intervals and distances (i.e. several hours and hundreds of km's). Although the assessment of the L84A1 grenade has been reduced to predicting the dispersion of a single species, SCIPUFF is equally capable of modelling the combined effect of many components when no single species is dominant.

SCIPUFF facilitates input of a comprehensive range of scenario description parameters, while its fundamental output is a 3 dimensional, temporally variant concentration map. Integrating throughout the screen duration, dosage at any point can be determined. The output also incorporates a probabilistic component to account for random atmospheric fluctuations. The UK executed a series of field trials to confirm the validity of the application of SCIPUFF to this short range domain.

A safety assessment is made by inspection of the downwind dosage variation. Based on toxicological considerations, the minimum safe distance from the detonation point is where D(x,y,z) is equal to D_{STEL}. At this point the dosage received is at the limit and therefore only one such exposure could be tolerated. Moving further downwind, the dosage decreases, therefore a number of such exposures as given by $D_{STEL}/D(x,y,z)$ may be tolerated. This type of analysis would be used to determine a safe distance for a trainer who may have to be present at many such incidents, although as the dosages become lower a more appropriate limit may be selected such as the TWA.

To quantify the hazards from a single grenade, simulations were carried for a number of meteorological conditions. The range of conditions encountered considered variations in wind speed and atmospheric stability. The grenade was approximated to a point source evolving the airborne products uniformly for 30 seconds from ground level.

The following figures relate to the dispersion of phosphoric acid at a height of 1.8m for moderate weather conditions; namely a wind speed of 4.1ms^{-1} (along the x axis) and neutral stability conditions. Figure 2 shows the mean H_3PO_4 concentration map corresponding to 120 seconds after detonation of the grenade. (Note: the black triangle represents the detonation point.)

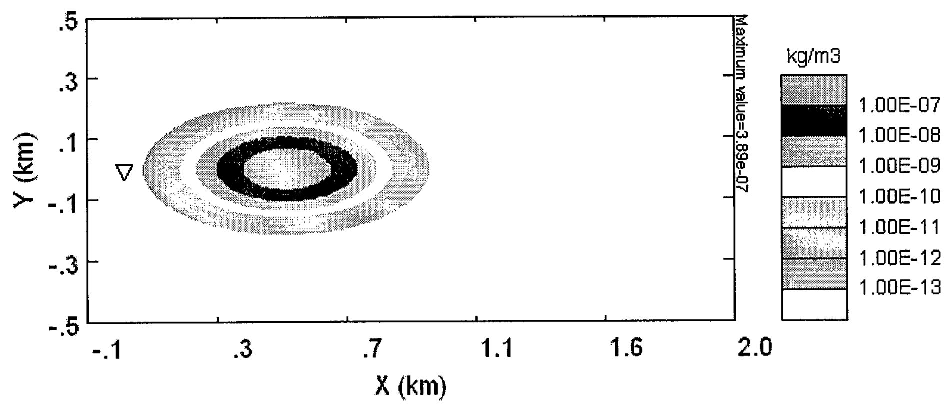

Figure 2 – Mean H_3PO_4 concentration map at t=120 seconds

Integrating over the duration of the screen, figure 3 is the phosphoric acid dosage map, with an automatic scaling of the contour levels.

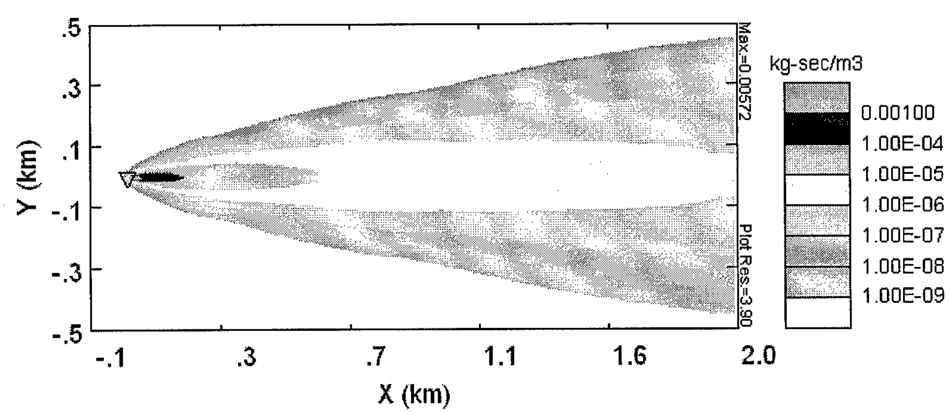

Figure 3 –H_3PO_4 dosage map (autoscale)

Figure 4 presents the same data set as figure 3, but on an expanded scale and with a single threshold level set equal to D_{STEL}. Therefore, the shaded area of figure 4 indicates where the exposure safety limit is exceeded.

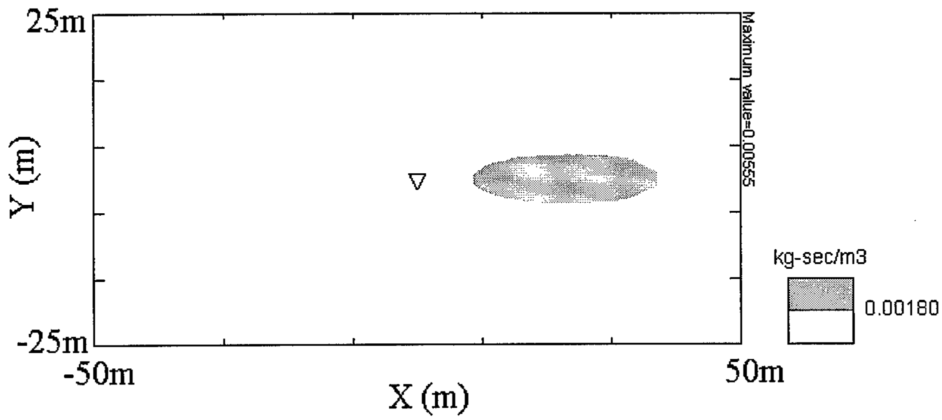

Figure 4 – H_3PO_4 dosage map (single threshold equal to D_{STEL})

7. DISCUSSION

This report has outlined the UK toxicological hazard assessment techniques, using the L84A1 hand thrown smoke grenade as an example.

The first stage of the assessment requires identification and quantification of all airborne products of combustion. This was achieved by direct analysis of the smoke cloud using a Parr bomb system to contain all the products of combustion. A total of 34 species were identified as airborne products of combustion. Two species were found to be dominant, namely H_3PO_4 and HCl, although this in itself is not grounds neglecting the other species. In order to reduce the number of species to be considered, an estimation of initial concentration was made, and compared with the corresponding OEL. Any species whose estimated concentration was significantly less than the OEL was neglected from further consideration. The results of this technique highlighted than H_3PO_4 was the primary threat and that controls set in place for this would be sufficient to protect against the other chemicals identified.

SCIPUFF was used to model the atmospheric transport of H_3PO_4, under a range of atmospheric conditions. Variations in atmospheric stability and wind speed were shown to have significant effect on safety templates, As an example of this assessment, figures relating to a wind speed of $4.1ms^{-1}$ with neutral atmospheric stability were presented. Figure 4 shows that under these conditions the minimum safe downwind distance in relation the inhalation of the airborne products is approximately 35m. At this distance only one exposure could be tolerated. However, if more exposures were expected, the dosages maps could yield the distance at which a number of munitions could be tolerated (although, this would not necessarily use the same OEL threshold).

An assessment structured along the guidelines outlined in this paper will help in the development of procedures to control the risk, by the use of appropriate personal protective equipment and restrictions/guidelines on usage.

It must be emphasised that interpretation of the inhalation assessment of the L84A1 hand thrown smoke grenade is subject to ratification by the UK medical/toxicological authority.

8. CONCLUSIONS

This paper has demonstrated how the UK use a combination of laboratory analysis techniques and numerical simulation methods, in conjunction with OELs, as the foundation of a toxicological hazard assessment process for obscurant munitions. The end product of this process is a series of safety templates, such that the exposure thresholds are not exceeded for a range of likely meteorological conditions. In conducting such an assessment, consideration needs to be given to the following areas:

- Personnel to be exposed (military or civilian)
- Number/frequency of exposures (trainer v trainee)
- Political circumstance (regular occurrence or 'one off')

The issues raised by these topics will effect the chosen safety limit, for e.g. STEL or TWA. Depending on the current political climate and the proposed region of use, consideration of the various circumstances listed above, may determine that the published occupational exposure limits are not the most appropriate threshold to determine the safe operating conditions relating to the use of obscurant systems. However, even in such a case, the process would remain the same and would simply require substitution of the appropriate limiting dosage threshold.

Once the inhalation risk has been considered, other hazards to personnel and the environmental issues need to be considered, in order to complete the toxicological and environmental impact assessment.

9. REFERENCES

[1] RICE P., *Guidelines for toxicity testing of smokes and pyrotechnic mixtures*, DERA/CBD/MC/CR96026/1.0, September 1996.

[2] GUPTA M. L., HUTCHINSON C. J., MERCER A. J., NORRIS V. J., Chemical analysis of smoke aerosols and residues, *The Smoke/Obscurants Symposium XX*, 28-30 April 1998.

[3] Health and Safety Executive (HSE), *Occupational Exposure Limits. Guidance Note EH40/98*, 1998.

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